PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) SINTERED FERRITE HAVING A GARNET STRUCTURE FOR HIGH FREQUENCY

We, MATSUSHITA ELECTRIC INDUSTRIAL COMPANY, LIMITED, a corporation organized under the laws of Japan, of No. 1006, Oaza Kadoma, Kadoma City, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly des-cribed in and by the following statement:—

This invention relates to a ferrite and more particularly to a ferrite having a garnet-type crystal structure which is useful for a magnetic material in the high frequency region, and to a process for preparing the same.

Generally, it is required that a magnetic material utilized in the high frequency region has a sufficiently high Curie temperature (T.) and a small half-line width of ferro-magnetic resonance absorption ΔH to sharply absorb 20 the electromagnetic wave of the resonance absorption frequency.

Various ferrites useful in the ultra high frequency region are known, some of which are spinel-type ferrites such as Mg-Al system 25 or Mg-Mn-Al system ferrites, and garnet-type ferrites such as Y-Al system or Y-Ga system

The half-line width of the above-mentioned conventional ferrites is about 100 Oe. A garnet-type ferrite comprising Y2O3, CaO, Fe₂O₃, InO₂ and V₂O₅ has been proposed and has been found useful as a magnetic material in the high frequency region. However, difficulty has been encountered in utilizing yttrium 35 and indium because of their high costs.

This invention resides in a garnet comprising Y₂O₃, CaO, Fe₂O₅, TiO₂ and V₂O₅ and represented by the formula;

$(Y_{3-2x-y}Ca_{2x+y})$ $(Fe_{5-x-y}Ti_yV_x)O_{12}$

where x is greater than 0 and less than 1.5. and 2x+y is greater than 0 and less than

As is apparent from the above formula, the ferrite of this invention does not include any high cost materials such as indium, so

that the particular ferrite is extremely economical. It is important that the ferrite of this invention has a small half-line width and sufficiently high Curie temperature. Furthermore, the ferrite has a small saturation magnetization less than 1900 gauss and a suffi-ciently high Curie temperature. These desired characteristics are achieved only by selecting the values of x and y in the above-mentioned

It should be noted that the half-line width of ferromagnetic resonance absorption of a ferrite closely depends upon its magnetic anisotropy and its porosity. Namely, the half-line width ΔH is the sum of the half-line width resulting from the magnetic anisotropy ΔH₁ and another half-line width ΔH₂, which half-line widths AH1 and AH2 are expressed by the following formulas:

$$\Delta H_1 = \frac{2.07G(2K_1/M_s)^2}{4\pi M_s}$$
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$$\Delta H_2 = 1.5(4\pi M_s)P (|K_1|/M_s < < 4\pi M_s)$$

where K₁ is a magnetic anisotropy constant, P is a porosity constant, G is a factor of about 1, and M_s is the saturation magnetisation (EMU/cc).

Therefore, it is preferable to use a ferrite having a small anisotropy constant and a small porosity.

The ferrite according to this invention has a low value of K₁/M₈ by virtue of the selected values of x and y so as to decrease the half-line width ΔH , and can be given a low porosity by a suitable process including sintering as described hereinbelow.

The process for preparing the garnet

according to this invention comprises mixing Y₂O₃, CaCO₃, Fe₂O₃, TiO₂ and V₂O₅, in proportions such as to provide molar ratios of the metals in the finished garnet, calcining the mixture, grinding the calcined material into fine particles, moulding said particles by means of pressing, extruding etc. and



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sintering the moulded material. The process will be more apparent from the description in

the examples given below.

The accompanying drawing shows saturation magnetization characteristics of several ferrites embodying the invention, as a function of temperature, wherein the ordinate represents the saturation magnetization and the abscissa the absolute temperature. In the 10 drawing, curves 1, 2 and 3 represent the saturation magnetization characteristics of ferrites corresponding to x=1, Y=0.5; x=1, y=0.3; and x=1, y=0.2, respectively.

The ferrite of this invention is easily

15 moulded as desired and cleanly finished so as to obtain a clean surface resulting in a

small half-line width.

Furthermore, the crystallized ferrite is much more economical than Y-Al or Y-Ga system ferrites, because it contains only a small

amount of costly yttrium.

The ferrite can be widely utilized for a filter, circulator, isolator, phase-shifter, or the

like.

Various further features and advantages of the invention will appear from the examples given below.

EXAMPLE I

A garnet-type ferrite $Y_{0.5}$ $Ca_{2.5}$ $Fe_{3.5}$ $Ti_{0.5}$ $V_{1.0}$ O_{12} (x=1, y=0.5) was prepared, which contained the following constituents:

	Y_2O_3	0.75 ^{male}
	CaO	2.50
	Fe ₂ O ₃	5.25
35	TiO ₂	1.00
	V_2O_5	2.00

A given quantity of starting materials Y2O3, CaCO₃, Fe₂O₃, TiO₂ and V₂O₅ was mixed together and maintained at a temperature of 550°C in the air for one hour and thereafter calcined at a temperature of 950°C for 12 hours in order to remove volatile matters or gases, including carbon dioxide dissociated from the calcium carbonate. The calcined 45 mixture was ground by means of a ball mill into fine particles and calcined at a temperature of 1150°C in any oxygen atmosphere for 6 hours. This calcined mixture was ground into fine particles having particle diameters of about 10 microns, and thereafter moulded to form sample elements and finally sintered at a temperature of 1350°C under an oxygen atmosphere for 24 hours. Each crystal structure of the resulting sample elements was identified as a single phase of garnet-type, by X-ray analysis. The ratio of the apparent density to the theoretical density of the resulting element was more than 95 percent.

0.75 mm diameter spheres were made of this sintered material and had a half-line width AH nearly equal to 35 Oe. at room temperature, measured at 9 GHZ. The saturation magnetization was nearly equal to 240 gauss at room temperature and the Curie temperature was 142°C.

EXAMPLE II

In this example, a ferrite $Y_{1.1}$ $Ca_{1.0}$ $Fe_{3.0}$ $Ti_{0.3}$ $V_{0.8}$ O_{12} (x=0.8, y=0.3) was prepared by utilizing the same procedure in Example I, but contained the following constituents:

> 1.65mole Y₂O₃ 1.90 CaO Fe₂O₃ 5.85 TiO2 0.60 2.00 ℧₂℧ℴ

The spherical samples were prepared and magnetic characteristics were measured and obtained as follows:

saturation magnetization $4\pi M_s$ at room temperature=530 gauss, half-line width of ferromagnetic resonance ΔH at room temperature=30 Oe., Curie temperature T_o=137°C.

EXAMPLE III

A ferrite $Y_{1.9}$ Ca_{1.1} Fe_{4.2} Ti_{0.5} V_{0.3} O₁₂ (x=0.3, y=0.5) was prepared which contained the following constituents:

Y_2O_3	2.85 ^{mole}	
CaO	1.10	
Fe ₂ O ₃	6.30	90
TiO ₂	1.0	
V_2O_5	0.35	

A mixture of the starting materials was calcined at 950°C in the air for 12 hours and then ground into fine particles. The fine particles were again calcined for 10 hours at 1180°C in an oxygen atmosphere. Then, the calcined mixture was again ground, moulded and thereafter sintered at 1350°C in an oxygen atmosphere for 6 hours.

The apparent density of the resultant was 0.965 times the theoretical density thereof.

The magnetic characteristics were as

saturation magnetization 4mMe at room 105 temperature =1340 gauss, half-line width of ferromagnetic resonance AH at room temperature=50 Oe., Curie temperature=180°C.

EXAMPLE IV

A ferrite $Y_{0.1}$ $Ca_{2.0}$ $Fe_{3.3}$ $Ti_{0.5}$ $V_{1.2}$ O_{12} (x=1.2, y=0.5) was prepared by the same procedure as Example I, which ferrite contained the following constituents:

Y ₂ O ₃	0.15 ^{mole}	115
CaO	2.90	
Fe ₂ O ₃	4.95	
TiO ₂	1.00	
V ₂ O ₅	3.00	

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The characteristics of the resultant were as follows:

saturation magnetization 4πM_o at room temperature=82 gauss, half-line width of ferromagnetization resonance ΔH at room temperature=40 Oe.,
Curie temperature T_o=107°C.

WHAT WE CLAIM IS:—

1. A garnet comprising Y₂O₃, CaO, Fe₂O₃,

TiO₂ and V₂O₅, and represented by the formula;

 $(Y_{3-2x-y}Ca_{2x+y})$ $(Fe_{5-x-y}Ti_yV_x)O_{12}$

where x is greater than 0 and less than 1.5, and 2x+y is greater than 0 and less than 3.

2. A process for preparing a garnet of claim

1, comprising mixing Y_2O_8 , CaO, Fe₂O₃ TiO₂ and V_2O_6 , in proportions providing the molar ratios of the metals required in the finished garnet, calcining the mixture, grinding the calcined material into fine particles, moulding said fine particles, and sintering the moulded particles.

3. A garnet comprising Y₂O₃, CaO, Fe₂O₃, TiO₂ and V₂O₅ substantially as hereinbefore described with specific reference to the foregoing Examples.

4. A process for preparing a garnet comprising Y₂O₃, CaO, Fe₂O₃, TiO₂ and V₂O₆ substantially as hereinbefore described with specific reference to the foregoing Examples.

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1 SHEET

This drawing is a reproduction of the Original on a reduced scale

